



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C11D 3/06</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 00/23552</b> <b>(43) International Publication Date:</b> 27 April 2000 (27.04.00)
<b>(21) International Application Number:</b> PCT/US99/24512 <b>(22) International Filing Date:</b> 19 October 1999 (19.10.99)  <b>(30) Priority Data:</b> 09/176,351                      21 October 1998 (21.10.98)                      US  <b>(71) Applicant:</b> DONLAR CORPORATION [US/US]; 6502 South Archer Road, Bedford Park, IL 60501 (US).  <b>(72) Inventors:</b> FAN, Lai-Duien, Grace; 1165 Berkley Road, Lake Zurich, IL 60047 (US). FAN, Joseph, C.; 1165 Berkley Road, Lake Zurich, IL 60047 (US).  <b>(74) Agents:</b> CEPURITIS, Talivaldis et al.; Olson & Hierl, Ltd., 20 North Wacker Drive, 36th Floor, Chicago, IL 60606 (US).		<b>(81) Designated States:</b> AU, BR, CA, JP, MX, NO, ZA, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> INHIBITION OF METAL CORROSION  <b>(57) Abstract</b>  A composition and method is disclosed for inhibiting the corrosion of metals in contact with an aqueous system capable of corroding the metal. The inventive composition contains a substantially water-soluble polymer of an acidic amino acid and at least one water-soluble salt of molybdenum or zinc. The composition is substantially non-toxic and environmentally acceptable and is supplied in a corrosion-inhibition amount to the otherwise metal-corrosive aqueous system.		

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## INHIBITION OF METAL CORROSION

### Technical Field

This invention relates to a composition and method for inhibiting the corrosion of metals in an aqueous system. More particularly, the invention is  
5 directed to the use of a substantially water-soluble, polymer of an acidic amino acid and at least one water-soluble salt of molybdenum or zinc.

### Background of the Invention

The corrosion of metal equipment is a widespread and expensive problem in many industrial settings such as open recirculating cooling towers and in the  
10 agricultural industry in fertilizer storage and irrigation systems. Expenses arise due to corrosion from lost production time and from costly repairs and replacement of metal equipment parts that have been weakened or destroyed by the action of water and oxygen at the metal surface.

Many environmental factors can accelerate the corrosion rate of metals, and  
15 ferrous metals in particular, in aqueous systems. For example, a high content of dissolved oxygen in an aqueous system has a significant oxidative influence on the corrosion rate of many metals. Inert gas purging or blanketing of aqueous systems can minimize the oxygen content of the aqueous solution to decrease the rate of corrosion, but this approach is limited to closed systems. Another factor is the  
20 temperature of the aqueous system. A reduction in the temperature of the aqueous system can decrease the rate of corrosion providing the reduced temperature can be tolerated and controlled. Similarly, a reduction in the velocity or movement of the aqueous system through the equipment can also reduce the rate of corrosion. However, some flow is essential to maintain corrosion protection when utilizing  
25 corrosion inhibitors. Finally, maintaining a pH value of about 7 units or greater in the aqueous system can lessen the corrosion rate of metals caused by acid attack.

Another important means of retarding corrosion in aqueous systems is the use of various chemical additives as "corrosion inhibitors." It is believed that these additives inhibit the rate of corrosion by forming surface films which physically block  
30 the diffusion of ions to and from the surface of the metal. Some of these corrosion inhibitors are organic polymers, others are salts of toxic metals such as chromium, still others are phosphorous-containing complexes. See, for example, Little et. al., "Corrosion Inhibition by Thermal Polyaspartate," Surface Reactive Peptides and

Polymers: Discovery and Commercialization, Sikes, C.S. and Wheeler, A.P. (Eds.), ACS Symposium Series No. 444 (1990). However, many of these chemical additives have a negative environmental impact given their toxicity and persistence.

5 In industrial water treatment applications, such as open recirculating cooling systems, and boilers, the formation of scale and corrosion is a major problem. The growth of mineral crystals (scale formation) on heat transfer surfaces leads to decreased heat transfer efficiency and increases corrosion of heat transfer components. Corrosion of the heat transfer components can lead to costly replacements and failures. The addition of chemicals to reduce scale is well known.

10 In many cases, phosphorus-containing materials are used to inhibit scale. However, when released into the environment, many of these materials can have a negative environmental impact. Polymeric organic inhibitors of scale are also known, such as polyacrylic acid, polymaleic acid, copolymers of acrylic and maleic acid, copolymers of acrylic acid and acrylamide, and the like. These polymeric materials, while being

15 good scale inhibitors, are not known to have corrosion inhibition activity. Moreover, these materials are also not readily biodegradable, and thus can contribute to the overall chemical burden on the environment for long periods of time.

The performance of polymers as mineral scale inhibitors is dependent on the ability of the polymers to interact with growth sites on the surface of growing mineral

20 crystals to retard mineral formation and reduce the adherence of the mineral to heat transfer surfaces by changing the crystal morphology.

Therefore, a need exists for an effective and environmentally tolerable polymeric corrosion inhibitor that can be used to inhibit corrosion and mineral scale on metal in contact with a metal-corrosive aqueous systems. Some previous attempts

25 to fulfill this need employed a solution containing aspartic acid homopolymers to inhibit the corrosion of metals in aqueous systems of basic pH (U.S. Patent No. 4,971,724 to Kalota et al.); an aqueous detergent solution combined with homopolymers of aspartic acid or glutamic acid (U.S. Patent No. 5,531,934 to Freeman et al.); and polyaspartate salts having alkali or alkaline earth metal

30 counterions as corrosion inhibitors in an aqueous saline environment (U.S. Patent No. 5,607,623 to Benton et al.). However, corrosion inhibition has met with limited success.

The present invention provides for both scale and corrosion inhibition benefits in a single, substantially non-toxic, environmentally acceptable polymer-containing composition.

#### Summary of the Invention

5        A composition and method for inhibiting corrosion of metals in contact with an aqueous system capable of corroding the metal is provided. The inventive method comprises supplying to the aqueous system a metal corrosion-inhibiting amount of a composition comprising a substantially water-soluble polymer of at least one acidic amino acid and at least one water-soluble salt of molybdenum or zinc.

10       The present inventive composition and method surprisingly is effective in inhibiting both corrosion and mineral scale on metal, particularly ferrous metal, in contact with an otherwise metal corrosive aqueous systems.

      The acidic amino acid polymers useful in the compositions and methods of the present invention are biodegradable, have low toxicity, have low calcium  
15       sensitivity, provide scale control, and provide corrosion control. Acidic amino acid polymers, in combination with water-soluble molybdate salts, zinc salts, and mixtures thereof, beneficially provide unexpectedly improved corrosion control without sacrificing the beneficial attributes of the polymers. Surprisingly, the corrosion  
20       inhibiting effect of the inventive composition is significantly greater than the mere additive corrosion inhibiting effect of the individual components.

      The compositions and methods of the present invention beneficially inhibit mineral scale and in particular, provide both scale and corrosion inhibiting  
25       functionality in a single composition. It is very common for both mineral scale and corrosion to be problems in the same application or system and conventionally require the use of multiple compositions to alleviate both scale and corrosion.

      The inventive compositions and method are particularly suitable for use in metal corrosive aqueous systems encountered in such industrial water treatment  
30       applications as open recirculating cooling towers, boilers and the like and in such agricultural applications as agricultural fertilizer systems, agricultural irrigation systems and the like.

      In the agriculture industry, in particular, the storage and application of fertilizer solutions can be problematic due to the corrosive nature of such fertilizer solutions to metals such as mild steel. The present invention provides effective and

environmentally acceptable compositions and methods for the inhibition of corrosion of metals in contact with known metal-corrosive aqueous fertilizer solutions.

Particular preferred compositions comprising a substantially water-soluble acidic amino acid polymer, particularly polyaspartate, and at least one water-soluble molybdate or zinc salt, were found to inhibit the corrosion of mild steel in the presence of an aqueous solution of a fertilizer, such as urea and ammonium nitrate.

An additional benefit of the inventive compositions can be realized in the agriculture industry since they can concurrently supply acidic amino acid polymers, which can also enhance plant productivity, as disclosed in U.S. Patent No. 5,350,735 to Kinnersley, et al., and the micro nutrient plant minerals, molybdenum or zinc or both.

#### Detailed Description of the Preferred Embodiments

The terms "acidic amino acid polymer," or any grammatical variations thereof, and "poly(aminoacids)" are used interchangeably and shall include the homopolymer and copolymers of the acid form of the amino acid as well as their salts. The salts of the acidic amino acid polymers may be alkali metal salts, alkaline earth metal salts, ammonium salts  $C_1-C_{20}$ , alkyl ammonium salts or aryl ammonium salts. The term "polymer" as used herein includes homopolymers and copolymers of acidic amino acid. The term "copolymer" as used herein includes random and block copolymers of acidic amino acid and their salts.

The inventive compositions contain a biodegradable and substantially non-toxic corrosion inhibiting amount of at least one substantially water-soluble polymer of an acidic amino acid together with at least one substantially water-soluble molybdate or zinc metal salt. The term "molybdate salt" as used herein defines a substantially non-toxic, water-soluble inorganic metal salt of molybdenum having the general formula (I):  $(X)_n(MoO_4)_m$ , wherein X is a cation, n and m are integers and the cationic charge on X times n is equal to 2m. The term "zinc salt" as used herein defines a substantially non-toxic water-soluble inorganic metal salt of zinc having the general formula (II):  $(Zn)_p(Y)_q$ , wherein Y is an anion, p and q are integers and the anionic charge on Y times q is equal to 2p. For convenience, the term "metal salt" is used herein to refer to molybdate and zinc salts.

Preferably, the molybdate salt has an alkali metal cation and most preferably is sodium molybdate ( $Na_2MoO_4$ ). Preferably, the zinc salt has an anion derived from

an inorganic mineral acid and most preferably is zinc chloride ( $\text{ZnCl}_2$ ) or a hydrate thereof.

Surprisingly, the corrosion inhibiting effect of the inventive compositions is considerably greater than the additive corrosion inhibiting effect, if any, attributable to the individual components.

Particularly preferred acidic amino acid polymers are synthesized from acidic amino acids, such as aspartic acid, in either  $\alpha$  form,  $\beta$  form, or optionally containing a cyclic imide (succinimide), as well as glutamic acid in either  $\alpha$  form, or  $\gamma$  form, or a derivative thereof. Preferably, the molecular size of the acidic amino acid polymer is in the range of about 1,000 to about 100,000 daltons, more preferably in the range of about 1,000 to about 20,000 daltons. The acidic amino acid residue content of the polymer is preferably in the range of about 20 mole percent to about 100 mole percent.

Preferably, the acidic amino acid polymer is a homopolymer of polyaspartic acid, or polyglutamic acid or is a block or random copolymer containing:

- a) at least one amino acid derived moiety selected from the group consisting of aspartic acid and glutamic acid; and
- b) one or more co-monomers selected from the group consisting of polybasic carboxylic acids and anhydrides, fatty acids, polybasic hydroxycarboxylic acids, monobasic polyhydroxycarboxylic acids, aliphatic amines, diamines and triamines, polyamines, carbohydrates, sugar carboxylic acids, amino acids, non-protein forming aminocarboxylic acids, lactams, lactones, diols, triols, polyols, unsaturated monocarboxylic, dicarboxylic and tricarboxylic acids, derivatized aspartic acid residues, derivatized glutamic acid residues; and the sum of the residues of aspartic acid, glutamic acid or mixture thereof comprises at least about 20% of the total number of residues in the polymer.

Acidic amino acid polymers useful in the compositions and methods of the present invention can be synthesized by any of numerous methods known in the chemical arts. See, for example, Koskan et al.; U.S. Patent Nos. 5,057,597; No. 5,116,513; No. 5,219,952, and No. 5,221,733, the disclosures of which are incorporated by reference, which describe methods for the manufacture of polysuccinimide and polyaspartic acid. Other methods can be found in U.S. Patent No. 5,142,062 which describes the use of phosphoric anhydride to facilitate the

polymerization of aspartic acid to polysuccinimide. Polyaspartic acid salts are obtained by the alkaline hydrolysis of polysuccinimide.

5 Fujimoto et al. in U.S. Patent No. 3,846,380 describe the formation of modified polypeptides having hydrophobic and hydrophilic substituents as side chains obtained by reacting polysuccinimide with at least one primary or secondary aliphatic amine in a polar aprotic solvent and hydrolyzing the resulting polyamide derivative with alkali to produce polypeptides that are useful as surface active agents.

10 Reactions of polysuccinimide in an aqueous medium with aqueous ammonia or aqueous primary or secondary amines produces copolymers of aspartic acid ammonium salts and aspartamide units. For example, hydrolysis of polysuccinimide with aqueous ammonia affords a copolymer of aspartamide (a.k.a. asparagine) and ammonium aspartate units in a ratio of about 40:60 to about 60:40.

15 Acidic amino acid copolymers containing co-monomers such as polybasic carboxylic acids and anhydrides, fatty acids, polybasic hydroxycarboxylic acids, monobasic polyhydroxycarboxylic acids, aliphatic amines, diamines and triamines, polyamines, carbohydrates, sugar carboxylic acids, amino acids, non-protein forming aminocarboxylic acids, lactams, lactones, diols, triols, polyols, unsaturated monocarboxylic, dicarboxylic and tricarboxylic acids, can be made by any number of methods described in the literature.

20 See, for example, U.S. Patent No. 5,478,919, to Koskan et al., incorporated herein by reference, which describes a method of preparation of copolymers of polysuccinimide or polyaspartic acid by copolymerization of maleic or fumaric acid, ammonia and one or more amino, hydroxyl or carboxyl containing monomers; U.S. Patents to Wood, No. 5,510,427 which describes a method of preparing polyaspartate 25 copolymers by polymerization of maleic acid, and ammonia with a diamine or triamine, followed by hydrolysis with base; No. 5,494,995 which describes a method of preparing polysuccinimide copolymers by polymerization of maleic acid, ammonia and a polycarboxylic acid, and optionally with a diamine or triamine; and No. 5,484,860 which describes a method of preparing polyaspartate copolymers by 30 polymerization of maleic acid, ammonia and a polycarboxylic acid, and optionally with a diamine or triamine, followed by hydrolysis with base.

Also, U.S. Patent Nos. 4,696,981 to Harada describes the copolymerization maleic or fumaric acid, ammonia and one or more amino acids using microwave



heating, to form polysuccinimide copolymers; No. 4,892,733, to Bichon et al. describes copolymers of aspartic or glutamic acid with other natural amino acids; No. 5,747,635, to Kroner et al., describes a method of preparing copolymers of polysuccinimide and polyaspartic acid by copolymerization of aspartic acid with 99 to 0.1 mole % of one or more polybasic carboxylic acids, polybasic carboxylic acid anhydrides, fatty acids, polybasic hydroxycarboxylic acids, monobasic polyhydroxycarboxylic acids, diamines and triamines, polyamines, carbohydrates, sugar carboxylic acids, amino acids, non-protein forming aminocarboxylic acids, or by radically initiated graft polymerization of monoethylenically unsaturated carboxylic acids in the presence of polyaspartic acid; and No. 5,679,761 to Heuer et al. which describes copolymers of polyaspartate or polysuccinimide with iminodisuccinate units. The relevant portions of each of the foregoing patents are incorporated herein by reference.

Examples of co-monomers useful in the acidic amino acid co-polymers of the present invention include, but are not limited to, lactic acid, citric acid, glycolic acid, malic acid, tartaric acid, succinic acid, adipic acid, butanetetracarboxylic acid, gluconic acid, glucuronic acid, glucaric acid, aconitic acid, sulfosuccinic acid, phosphinosuccinic acid, phosphonosuccinic acid, iminodiacetic acid, iminodisuccinic acid, nitrilotriacetic acid, stearic acid, palmitic acid, cyclohexanedicarboxylic acid and anhydride, terephthalic acid, phthalic acid and anhydride, crotonic acid, sorbitol, glycerol, glucose, fructose, sucrose, maltose, glycine, alanine, serine, threonine, cystine, cysteine, ethylenediamine, diethylenetriamine, triethylenetetramine, polyamines, 1,6-diaminohexane, octadecylamine, 6-aminocaproic acid, 4-aminobutyric acid, diaminocyclohexane, urea, melamine, carbonyldiurea, hydrazine, ascorbic and isoascorbic acid, sorbic acid, maleic acid, cyanuric acid, alkylamines, alkyltriamines, acrylic acid, methacrylic acid, maleic acid, maleic anhydride, alkylmaleic acids, alkenylsuccinic acids and anhydrides thereof, and methylenemalononic acid. The term "alkyl" and "alkanyl" as used herein means that the alkyl or alkanyl group has 1 to 7 carbon atoms.

Examples of derivatized aspartic acid and derivatized glutamic acid residues include materials in which the free carboxyl group of the aspartic acid or glutamic acid residue has been chemically bonded with an amino, hydroxyl or mercapto containing moiety to form an amide, ester or thioester bond.

Non-limiting examples of acidic amino acid polymers containing derivatized aspartic acid or glutamic acid residues useful in the compositions and methods of the present invention are found in U.S. Patents to Uhr et al., Nos. 5,506,335 and 5,726,280 which describe polyaspartate alkyl and aryl amide derivatives with sulfonic acid group-containing side chains on the alkyl or aryl moieties; U.S. Patents to  
5 Jacquet et al., No. 4,363,797 which describes derivatized polyaspartates bearing amide, mercapto and sulfoalkylamide functional group bearing moieties attached to the polyaspartate by amide bonds to the free carboxyl groups of the polymer; and No. 4,314,808 which describes derivatized polyaspartates wherein alkyl substituents,  
10 functionalized alkyl substituents, dyes and dye precursors that are attached to the polyaspartate by amide bonds to the free carboxyl groups of the polymer; U.S. Patent No. 3,846,380 to Fujimoto, which describes derivatized polyaspartates wherein C<sub>1</sub> to C<sub>20</sub> alkyl groups, in proportions from 0.005 to 1 substituents per monomer unit, are attached to the polyaspartate by amide bonds to the free carboxyl groups of the  
15 polymer. The relevant portions of each of the foregoing patents are incorporated by reference.

Also, U.S. Patent No. 5,639,832, to Kroner et al, describes a method of derivatizing polysuccinimide with amino acids by reaction of polysuccinimide with amino acids in aqueous medium at pH values wherein at least 5 % of the amino acids  
20 are in the free amine (non-protonated) form; and PCT Application No. WO 96/04332, to Greindl et al., describes derivatives of polyaspartic acid having hydroxamic acid, hydroxamic ether and/or hydrazide groups in the side chain, formed by reaction of polysuccinimide with hydroxylamine, hydroxylamine alkyl ethers with 1 to 18 C atoms in the alkyl group, N-mono-hydroxylamines with 1 to 18  
25 C atoms in the alkyl group, and/or hydrazine in aqueous or alcohol media at pH values of at least 7. The relevant portions of each of the foregoing patents are incorporated by reference.

Examples of amino, hydroxyl or mercapto containing moieties that may be bonded with aspartic acid or glutamic acid residues to form derivatized aspartic acid  
30 or derivatized glutamic acid residues include, but are not limited to: hydrazine, C<sub>1</sub>-C<sub>20</sub> alkyl or aryl substituted hydrazines, hydroxyl amine, C<sub>1</sub>-C<sub>20</sub> alkyl O-substituted hydroxylamines, natural amino acids such as alanine, glycine, leucine, phenylalanine, lysine, non-natural amino acids such as 6-aminocaproic acid, 4-aminobutyric acid, 2-

aminobenzoic acid, 4-aminobenzoic acid, or iminodiacetic acid, C<sub>1</sub>-C<sub>20</sub> alkyl amines, aryl amines such as aniline, secondary alkyl amines such as dimethylamine, morpholine, diethylamine, or N-methylstearylamine, substituted alkyl or aryl amines such as taurine, 3-phosphinopropyl amine, or 4-aminobenzenesulfonic acid, 5 heterocyclic amines such as 2-aminopyridine, 2-aminopyrazine, 2-aminothiazole, or 2-aminoimidazole, diamines such as ethylenediamine, hexamethylenediamine, or alkoxylated diamines such as triethyleneglycol diamine, alkoxylated amines such as amine capped polyethylene oxides or amine capped polypropylene oxides, polyols such as ethylene glycol, propylene glycol, glycerin, polyethylene oxides, 10 polypropylene oxides, sugars, or amino sugars, thiols such as butanethiol, 2-hydroxyethanethiol, or 2-aminoethanethiol, and hydroxycarboxylic acids such as glycolic acid, lactic acid, 2-hydroxybutyric acid, citric acid, tartaric acid, or salicylic acid.

Preferred amino acids for preparing acidic amino acid polymers useful in the 15 present invention are aspartic acid, glutamic acid or mixtures thereof and the sum of the residues of aspartic acid or glutamic acid or both is at least about 20%, more preferably, at least about 30%, most preferably at least about 50% of the total number of polymeric residues.

The starting materials, i.e., the amino acids and other co-monomers, for the 20 polymerization to form the acidic amino acid polymers of the present invention can exist as optical isomers, depending upon their respective structures, and can be polymerized either as a racemic mixture or as segregated optical isomers.

The aspartic acid moieties of the acidic amino acid polymers of the present invention may be synthesized by any of several methods known in the art, such as 25 from the thermal polymerization of aspartic acid or of precursors of aspartic acid such as maleamic acid, fumaramic acid, ammonium salts of maleic acid, ammonium salts of fumaric acid and ammonium salts of malic acid. The acidic amino acid polymers can also be synthesized by microbial fermentation.

In agricultural applications to inhibit corrosion of metal equipment in contact 30 with fertilizer solutions, the inventive composition containing at least one molybdate or zinc salt and the acidic amino acid polymers can be supplied in the form of an aqueous solution or a substantially solid form. The weight ratio of the acidic amino

acid polymer to molybdate and zinc salts can be in the range of about 0.1:1 to about 1,000,000:1, preferably in the range of about 20:1 to about 100,000:1.

When supplied as an aqueous composition, the content, on a total composition basis, of acidic amino acid polymer preferably is in the range of about 0.001% (10 ppm) to about 10% (100,000 ppm) by weight and the content of the metal salt is in the range of at least about 0.00001% (0.1 ppm) to about 0.01% (100 ppm) by weight. More preferably, the inventive aqueous composition to be supplied has an acidic amino acid polymer content in the range of about 0.001% (10 ppm) to about 10% (100,000 ppm) by weight, a molybdate salt content of at least about 0.00001% (0.1 ppm) to about 0.001% (10 ppm) by weight or a zinc salt concentration of at least about 0.00001% (0.1 ppm) to about 0.0005% (5 ppm) by weight or a combined molybdate and zinc salt concentration of at least about 0.00001% (0.1 ppm) by weight. A most preferred composition has an acidic amino acid polymer content of about 0.5% (5000 ppm) to about 5% (50,000 ppm) by weight and at least one molybdate or zinc salt in about 0.0001% (1 ppm) to about 0.001% (10 ppm) by weight, i.e., a weight ratio range of about 500:1 to about 50,000:1. Preferably, the pH of the composition is in the range of about 6 to about 14 pH units.

Fertilizer solutions containing the inventive composition can also contain plant nutrients, such as potassium, phosphorus, nitrogen and sulfur. Most preferably, the fertilizer solution contains urea and ammonium nitrate (referred to as UAN). Such plant nutrients can be supplied together with the acidic amino acid polymer and at least one molybdate or zinc salt for agricultural uses. Advantageously, the molybdate salts and zinc salts useful in the inventive composition can provide, respectively, the plant micro nutrients, molybdenum and zinc. Preferably the the pH of the composition is in the range of about 6 to about 14 units, more preferably in the range of about 7 to about 9 units.

The compositions and method of the present invention are particularly useful in industrial water treatment applications such as open recirculating cooling towers, boilers and the like, where both scale and corrosion problems, particularly of ferrous metals, occur in the same system, simultaneously.

In an industrial aqueous system, the weight ratio of the acidic amino acid polymer to the at least one molybdate or zinc salt can be in the range of about 0.01:1 to about 1,000:1, preferably in the range of about 1:1 to about 500:1, more

preferably in the range of about 2:1 to about 25:1. Preferably, an industrial aqueous system will contain an acidic amino acid polymer content in the range of about 0.00001% (0.1 ppm) to about 0.01% (100 ppm) by weight and at least one molybdate or zinc salt in the range of about 0.00001% (0.1 ppm) to about 0.001% (10 ppm) by weight. A preferred composition contains, on a total composition weight basis, an acidic amino acid polymer content of about 0.0001% (1 ppm) to about 0.005% (50 ppm) by weight and molybdate or zinc salt content of about 0.00002% (0.2 ppm) to about 0.0005% (5 ppm) by weight, i.e., a weight ratio of polymer to salt of about 250:1 to about 0.2:1. A preferred pH range of the composition is about 6 to about 14 units.

Other common water treatment components, such as biocides, dispersants, sequestrants, other scale inhibitors or other corrosion inhibitors, and mixtures thereof may be supplied along with the acidic amino acid polymer and the molybdate or zinc salt in the inventive composition. Useful formulations, for examples, can contain polyaspartate, metal salts and phosphonate sequestrants, wherein the added phosphonate sequestrants may further enhance either the scale inhibition or corrosion activity of the formulation.

The scale inhibiting activity of poly(amino acids) is well known. One other useful feature of such amino acid polymers is low calcium sensitivity. Calcium sensitivity is the tendency of an inhibitor to precipitate as a calcium salt in waters having a high calcium hardness. Such precipitation is undesirable in that the precipitated inhibitor can no longer perform its intended function.

Calcium sensitivity may be measured in a relatively simple test wherein a known amount of inhibitor (typically enough to attain 50 ppm concentration in solution) is added to a water composition containing about 500 ppm of calcium (as calcium carbonate), 0.005M borate buffer at a temperature of about 70°C (about 158°F), pH 8.3 for an incubation time of about 18 hours. The turbidity of the solution is monitored using a nephelometer. Turbidity is measured in Nephelometric Turbidity Units (NTU). Turbidity is an indication of precipitation. Higher turbidity indicates high calcium sensitivity. In such a test, an amino acid polymer of polyaspartic acid, showed no measurable turbidity, whereas common non-amino acid based scale inhibitors such as polyacrylic acid and polymaleic acid had measureable

turbidities of 8 and 13 NTU, respectively, indicating low calcium sensitivity for polyaspartate and high calcium sensitivity for the polyacrylate and polymaleates.

The activity of corrosion inhibitors toward metal corrosion is commonly assayed by the Polarization Resistance Method, ASTM G-59, found in "Standard Practice for Conducting Potentiodynamic Polarization Resistance Measurements," American Society For Testing And Materials, Philadelphia, Pennsylvania, the disclosures of which are incorporated herein by reference. Linear Polarization Resistance is an electrochemical technique that measures the DC current ( $i_{meas}$ ) through the metal/fluid interface under study by applying a small electric potential difference ( $\Delta E$ ) from the corrosion potential ( $E_{corr}$ ).  $i_{meas}$  is related to corrosion current density ( $i_{corr}$ ) by the Stern-Geary equation:

$$\frac{\Delta E}{i_{meas}} = \frac{\beta_a \beta_c}{(2.303 i_{corr}) (\beta_a + \beta_c)}$$

where:  $\beta_a$  = Anodic Tafel Slope and  $\beta_c$  = Cathodic Tafel Slope.

The corrosion rate is directly proportional to the corrosion current density, and can be calculated using the ASTM G-102 standard method, found in "Calculation of Corrosion Rates and Related Information From Electrochemical Measurements," American Society For Testing And Materials, Philadelphia, Pennsylvania, the disclosures of which are incorporated herein by reference.

The following examples illustrate composition embodiments and the method of the present invention in agricultural fertilizer solutions and in industrial aqueous systems. The compositions and methods presented are illustrations of preferred embodiments and are not intended as limitations.

**Example 1: Inhibition of Steel Corrosion in an Aqueous Fertilizer Solution by Acidic Amino Acid Polymer and Zinc Salt.**

The corrosion rate of C1010 mild steel coupons submerged in an aqueous fertilizer solution was monitored using the Polarization Resistance Method. The analytical instrument contained a two-electrode probe which provided the corrosion rates as milli-inches per year (mpy).

The control sample was a 28% by weight aqueous solution of the commercial fertilizer, urea and ammonium nitrate (UAN), commonly employed in the agriculture

industry and is known to be metal corrosive, especially to ferrous metals. The corrosion rate of separate steel coupons was measured following immersion contact in a series of tests performed with the UAN fertilizer solution containing either thermal polyaspartate, (TPA), as the acidic amino acid polymer (5000 molecular weight, sodium salt form), or zinc chloride or TPA and zinc chloride and the results were compared to corrosion in contact with the control sample.

The concentration of the aspartic acid polymer in the test aqueous solutions ranged from about 1% (10,000 ppm) to about 0.001% (10 ppm) by weight and the concentration of zinc chloride was about 0.0002% (2 ppm) by weight as shown in Table 1 below. All compositions had a pH of about 8.4. Measurements were made at ambient room temperature over an immersion period of 4 to 28 days. The results are summarized in Table 1.

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Table 1. Corrosion Inhibition of Mild Steel

Day	UAN alone (28%)	1% TPA (10000 ppm)	Corrosion rate (mpy)									
			2 ppm		1%TPA + 2ppm		5000ppm		1000 ppm		50 ppm TPA	
			ZnCl <sub>2</sub>	ZnCl <sub>2</sub>	ZnCl <sub>2</sub>	ZnCl <sub>2</sub>	TPA + 2ppm ZnCl <sub>2</sub>	TPA + 2ppm ZnCl <sub>2</sub>	TPA + 2ppm ZnCl <sub>2</sub>	TPA + 2ppm ZnCl <sub>2</sub>	TPA + 2 ppm ZnCl <sub>2</sub>	10 ppm TPA + 2 ppm ZnCl <sub>2</sub>
1	0.3	0.7	0	0.1	0	0	0	0	0	0	0.1	0.1
2	0.1	0										
3	0.1	0										
4	80.4	0	0.1	0	0	0	0	0	0	0	0.1	0
5		0.1			0	0	0	0	0	0	0.1	0.1
6			0.1	0.1	0	0	0	0	0	0	0.1	0
7			0	0	0	0	0	0	0	0	0.1	0.1
8		2.4	0.1	0.1	0	0	0	0	0	0	0.1	0
9		2.8										
10		2.4										
11			0	0		0						0
12		2.6	0.1	0.1	0	0	0	0	0	0	0.1	0.1
13			90.8	0	0	0	0	0	0	0	0.1	0.1
14					0	0					0.1	0
15												
16												
17				0	0	0	0	0	0	0	0.1	0.1
18												
19												
20					0	0	0	0	0	0	0.1	0.1
21					0.1	0	0	0	0	0	0.1	0

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Table 1. Corrosion Inhibition of Mild Steel

Day	UAN alone (28%)	1% TPA (10000 ppm)	Treatment							
			Corrosion rate (mpy)							
			1%TPA + 2ppm ZnCl <sub>2</sub>	5000ppm TPA + 2ppm ZnCl <sub>2</sub>	1000 ppm TPA + 2ppm ZnCl <sub>2</sub>	50 ppm TPA + 2 ppm ZnCl <sub>2</sub>	25 ppm TPA + 2 ppm ZnCl <sub>2</sub>	10 ppm TPA + 2 ppm ZnCl <sub>2</sub>		
22				0.1	0	0	0.1	0.1		
23										
24										
25				0.2	0.2	0.1	0	0		
26				0.2	0.2	0.1	0.1	0.1		
27				0.2	0.2	0.2	0.1	0		
28				0.1	0.2	0.2	0.1	0.1		
29				0.2	0.2	0.2	0	0		

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The data in Table 1 clearly showed that corrosion inhibition by the combination of the polyaspartate with zinc salt was considerably more effective than that achieved with either the polymer alone or the zinc salt alone. The UAN control produced massive corrosion within 4 days (80.4 mpy). Polyaspartate (1%) alone decreased the corrosion rate during the first 7 days and produced "slight corrosion" (mpy value of 2.4-2.6) over 8-14 days, whereas massive corrosion (90.8 mpy) was produced with zinc salt (2 ppm) alone after by 13 days. With all the inventive compositions containing the combination of polyaspartate and zinc chloride, however, the corrosion rates surprisingly ranged from none (0 mpy) to at most about 0.2 mpy over the entire 29 day test period.

Similarly effective inhibition was achieved in similar tests conducted over a test period of 30 days, with 1 ppm zinc salt in combination with 10 ppm, 25 ppm, 50 ppm or 100 ppm polyaspartate.

Example 2. Corrosion Inhibition by Acidic Amino Acid Polymer and Molybdate Salt in a Fertilizer Solution.

The procedure of Example 1 was repeated, except that the UAN fertilizer (28 % by weight) compositions contained either 1% by weight of sodium polyaspartate, (5000 Mw), or 0.0005% by weight sodium molybdate (5 ppm) or a combination of 1% by weight sodium polyaspartate and 0.0005% by weight sodium molybdate at a pH of about 8.4. After 12 days of immersion contact, no corrosion (0 mpy) of the C1010 mild steel coupons was evident when the inventive composition containing the polymer and molybdate salt was used. In contrast, severe corrosion of the coupons was evident after 4 days immersion contact with the control sample (UAN only, 80 mpy) and after 7 days immersion contact with the sodium molybdate sample (87 mpy), whereas the aspartic acid polymer sample had only slight corrosion after 8-12 days (2.4-2.6 mpy).

Example 3. Corrosion Inhibition by Acidic Amino Acid Polymer with Molybdate and Zinc Salt in a Cooling Water Application.

Water used for cooling applications is typically described as scale forming or corrosive, primarily depending on the concentration of hardness ions in the water and the

alkalinity. Low hardness waters (low LSI), are usually significantly more corrosive than higher hardness waters (high LSI).

This example demonstrates corrosion inhibition by acidic amino acid polymer with molybdate and zinc salt in an aggressive soft water (substantially low LSI) containing  
5 about 35 ppm  $\text{Ca}^{+2}$  as  $\text{CaCO}_3$ , about 10 ppm  $\text{Mg}^{+2}$  as  $\text{CaCO}_3$  and about 25 ppm total alkalinity to simulate the cooling water used in open recirculatory cooling towers (hereafter, "cooling water"). Total alkalinity was determined as M-alkalinity (i.e., titration with acid to a Methyl Orange indicator endpoint). The cooling water had a pH  
10 of about 8.0 and a temperature of about 27°C (about 81°F). The cooling water was constantly purged with air to ensure oxygen saturation to simulate open recirculation tower conditions.

A series of separate tests were performed over a test run period of about 18 hours employing either cooling water (blank), or cooling water containing (0.001%) 10 ppm polyaspartate with and without zinc chloride or sodium molybdate salt in the amounts  
15 shown in Table 2. All tests were performed on C1010 mild steel coupons that had been pre-corroded in 1 N hydrochloric acid for about 10 minutes and then rinsed with deionized water to simulate tower metal use conditions. The flow rate during pre-corrosion and each test was about 1 m/s (3.3 ft/s).

The corrosion rate was determined by the Polarization Resistance Method as in  
20 Example 1 and by visually observing the appearance of the metal surface for pitting and general corrosion (rust). The results are presented in Table 2.

Table 2. The Corrosion Rate Of C1010 Mild Steel In Cooling Water With Various Treatments.

Treatment	Corrosion Rate (mpy)	Appearance, Observed Pitting
Blank	52	large amount of general corrosion (rust), pitting
10 ppm polyaspartate	2.5	large pits, reduced rust
10 ppm polyaspartate + 1 ppm $Zn^{+2}$	2.0	small pits, greatly reduced rust
10 ppm polyaspartate + 0.4 ppm $Zn^{+2}$	2.0	small pits, greatly reduced rust
10 ppm polyaspartate + 5 ppm $MoO_4^{-2}$	1.5	small pits, little rust
10 ppm polyaspartate + 0.4 ppm $Zn^{+2}$ + 5 ppm $MoO_4^{-2}$	1.6	small pits, very little surface rust
2 ppm $Zn^{+2}$	8.4	large pits

The data in Table 2 illustrate the efficacy of polyaspartate as a corrosion inhibitor and provides an indication of potential synergistic effects with molybdate in lowering corrosion rates and with zinc in reducing pitting corrosion. The advantages of combining polyaspartate with molybdate salts, zinc salt or both were depicted by comparing the surface morphologies of the treated coupons. The data in Table 2 clearly show that combinations of polyaspartate and zinc salt, for example, unexpectedly reduced corrosion attack and pitting was minimized relative to that of the zinc salt treatment. It is well known that at a low level of 1 ppm or less the corrosion rate of  $Zn^{+2}$  is greater than that at 2 ppm (i.e., 8.4 mpy). Thus, the combination of polyaspartate and  $Zn^{+2}$  advantageously achieved a low corrosion rate employing a

fraction of the zinc which would be needed if zinc were used alone to reduce the corrosion rate to the same level.

The combination of polyaspartate with molybdate salt or with a combination of zinc and molybdate salts resulted in a high level of inhibition of both general corrosion and pitting attack. It is well known that 5 ppm  $\text{MoO}_4^{2-}$  is not an effective corrosion inhibitor.

The potential Polarization data indicates that polyaspartate acts as an anodic inhibitor. Thus, the anodic Tafel slope of the mild steel coupon doubles when treated with 10 ppm of polyaspartate.

**WE CLAIM:**

1. A method for inhibiting the corrosion of metals in contact with a metal corrosive aqueous system which comprises supplying to the aqueous system a corrosion-inhibiting amount of a composition comprising a substantially water-soluble polymer of at least one acidic amino acid and at least one water-soluble metal salt selected from the group consisting of molybdate salts and zinc salts.
2. The method of claim 1 wherein the acidic amino acid is selected from the group consisting of aspartic acid, glutamic acid and mixtures thereof.
3. The method of claim 1 wherein the molecular size of the acidic amino acid polymer is in the range of about 1,000 to about 100,000 daltons.
4. The method of claim 1 wherein the acidic amino acid content comprises at least about 20% by weight of the polymer.
5. The method of claim 1 wherein the metal salt is sodium molybdate.
6. The method of claim 1 wherein the metal salt is zinc chloride.
7. The method of claim 1 wherein the metal salt comprises sodium molybdate, zinc chloride and mixtures thereof.
8. The method of claim 1, wherein, on a total composition weight basis, the supplied composition contains about 0.001% to about 10% by weight acidic amino acid polymer, and at least about 0.00001% by weight of the metal salt.
9. The method of claim 1 wherein the composition is supplied to an aqueous fertilizer system.
10. The method of claim 9 wherein the acidic amino acid polymer is an aspartic acid polymer.
11. The method of claim 9 wherein, on a total composition weight basis, the composition contains about 0.5% to about 5% by weight acidic amino acid polymer and about 0.00001% to about 0.001% by weight molybdate salt.
12. The method of claim 1 wherein the aqueous system has a pH in the range of about 6 to about 14.
13. The method of claim 1 wherein the aqueous system is useful for agricultural applications and the composition further includes plant nutrients.

14. The method of claim 1 wherein the aqueous system is a water treatment application.

15. The method of claim 1 wherein the composition supplied contains, on a total composition weight basis, about 0.00001% to about 0.01% by weight acidic amino acid polymer and at least about 0.00001% of the metal salt.

16. The method of claim 1 wherein the composition contains, on a total composition weight basis, about 0.0001% to about 0.005% by weight acidic amino acid polymer and at least about 0.00001% of the metal salt.

17. A method of claim 1 wherein the composition comprises an acidic amino acid copolymer comprising: (a) at least one amino acid derived moiety selected from the group consisting of aspartic acid, glutamic acid and mixtures thereof; and (b) one or more co-monomers selected from the group consisting of polybasic carboxylic acids and anhydrides, fatty acids, polybasic hydroxycarboxylic acids, monobasic polyhydroxycarboxylic acids, diphenyl amines, diamines, triamines, polyamines, carbohydrates, sugar carboxylic acids, amino acids, non-protein forming aminocarboxylic acids, lactams, lactones, diols, triols, polyols, unsaturated dicarboxylic and tricarboxylic acids, unsaturated monocarboxylic acids, derivatized aspartic acid residues, and derivatized glutamic acid residues; wherein the sum of the residues of aspartic acid, glutamic acid or mixture thereof comprises at least about 20% of the total number of residues in the polymer.

18. A composition suitable for use in the inhibition of corrosion of metal in contact with a metal corrosive aqueous system comprising a corrosion-inhibiting amount of a substantially water-soluble polymer of an acidic amino acid, and at least one water-soluble metal salt selected from the group consisting of molybdate salts and zinc salts.

19. The composition of claim 18 wherein the weight ratio of the acidic amino acid polymer to the metal salt is in the range of about 0.1:1 to about 1,000,000:1.

20. The composition of claim 18 wherein the weight ratio of the acidic amino acid polymer to the metal salt is in the range of 0.01:1 to about 1,000:1.

21. The composition of claim 18 wherein the composition is suitable for agricultural applications and includes fertilizer.

22. The composition of claim 18 wherein the acidic amino acid polymer is a copolymer comprising: (a) at least one amino acid derived moiety selected from the group consisting of aspartic acid, glutamic acid and mixtures thereof; and (b) one or more co-monomers selected from the group consisting of polybasic carboxylic acids and anhydrides, fatty acids, polybasic hydroxycarboxylic acids, monobasic polyhydroxycarboxylic acids, aliphatic amines, diamines and triamines, polyamines, carbohydrates, sugar carboxylic acids, amino acids, non-protein forming aminocarboxylic acids, lactams, lactones, diols, triols, polyols, unsaturated dicarboxylic and tricarboxylic acids, unsaturated monocarboxylic acids, derivatized aspartic acid residues, and derivatized glutamic acid residues; wherein the sum of the residues of aspartic acid, glutamic acid or mixture thereof comprises at least about 20% of the total number of residues in the polymer.

23. The composition of claim 18 wherein the acidic amino acid polymer is polyaspartate.

24. The composition of claim 18 wherein the metal salt is sodium molybdate.

25. The composition of claim 18 wherein the metal salt is zinc chloride.

26. The composition of claim 18 in a substantially solid form.

27. The composition of claim 18 in an aqueous solution form.

28. The composition of claim 18 further including water treatment components selected from the group consisting of biocides, dispersants, sequestrants and mixtures thereof.



## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US99/24512

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) : C 11D 3/06

US CL : 252/389.52, 389.54; 210/701

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/389.52, 389.54; 210/701

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, 5,531,934 (FREEMAN et al) 02 July 1996. See col. 1, lines 6-10; col. 2, lines 12-20, 45-57; col. 5, lines 13-23; col. 6, lines 5-68; col. 7, lines 60-65; col. 8, lines 58-61; claims 5-7.	1-28

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:	* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

22 DECEMBER 1999

Date of mailing of the international search report

10 FEB 2000

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

CEPHIA D. TOOMER

Telephone No. (703) 308-0661

DEBORAH THOMAS  
PARALEGAL SPECIALIST

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